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COMBINATION BASED ON MICROFIBRILS AND MINERAL  
PARTICLES, PREPARATION AND USES

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The present invention relates to a

- 5 combination in dry form, on the one hand comprising microfibrils, and on the other comprising mineral particles.

The present invention similarly relates to a method of preparation and to the use of such a

- 10 combination in compositions comprising polymers.

The term "polymers" is intended to denote both polymers and copolymers, including elastomers, thermoplastic polymers, alloys thereof or blends thereof.

- 15 This is found to be particularly advantageous in the case of compositions predominantly comprising elastomers crosslinked by any means known to those skilled in the art (peroxides, sulphur, etc.).

- The use of fibres in elastomer-based  
20 compositions is known but remains relatively undeveloped. The reason for this is that although the introduction of short fibres, such as Santoweb fibres, into such compositions improves the rigidity of the material to which these short fibres are added, it  
25 nevertheless affects the breaking strength and fatigue strength thereof. Thus, it is not possible to achieve a

satisfactory compromise of properties.

Recently, the idea has arisen of preparing elastomer-based compositions containing smaller-sized fibres, such as Kevlar pulp comprising partially defibrillated fibres. In this case, the rigidity properties are improved compared with those obtained with short fibres, in particular as regards the final properties of the material. However, it appears that the fatigue strength is adversely affected. In addition, there is a problem of redispersion of these fibrils in the elastomer composition, which makes it necessary for them to be incorporated into the composition while this composition is in the form of a latex.

It thus appears that it is possible to improve the compromise of properties by changing the morphology of the fibres used: however, this approach comes up against a problem of redispersion of these fibres in the polymer matrix.

The aim of the present invention is in particular to solve this problem of redispersion.

The invention consists of a specific combination, comprising microfibrils, which is easy to disperse in polymer compositions, including thermoplastic polymers or elastomers, irrespective of the form in which these compositions are found (latex

or non-latex).

In addition, and this constitutes a considerable advantage of the present invention, the compositions thus supplemented with additive, which  
5 also form part of the invention, have very surprising mechanical properties. Thus, for a vulcanized (sulphur-crosslinked) elastomer, firstly, a significant increase in the secant modulus (relative to the deformation stress) and in the stress, more particularly between  
10 about 50% and 300% deformation, are observed. Furthermore, contrary to what was rightly to be expected, in this case, the final properties of the material thus supplemented with additive, for example such as the breaking strength, are not adversely  
15 affected. Secondly, the viscoelastic behaviour of the material obtained is just as surprising. A person skilled in the art expected to observe an increase in the dissipation of energy after addition of microfibrils. This is not the case when they are  
20 incorporated into the elastomer by means of the combination according to the invention.

Thus, a subject of the present invention is a combination in dry form comprising:

- microfibrils with a mean diameter of  
25 less than 0.8  $\mu\text{m}$ , and
- at least one mineral particle.

Another subject of the present invention consists of a process for obtaining this combination, which consists in preparing a suspension comprising the microfibrils and at least one mineral particle, which  
5 is then dried.

Similarly, a subject of the present invention is the use of the combination according to the invention in polymers, in particular in thermoplastic polymers and elastomers, alloys thereof or blends  
10 thereof.

Finally, the invention relates to polymer-based articles comprising the combination according to the invention.

It has been found, entirely unexpectedly,  
15 that a combination based on the microfibrils as defined above, combined with mineral particles, can be incorporated easily and homogeneously into formulations based on elastomers or polymers.

This is because the combination according to  
20 the invention is very easy to use, given the fact that it is in a dry, i.e. solid, form and more particularly in the form of individualized solid (powder, essentially spherical beads, granules). Furthermore, the combination can be incorporated into a polymer  
25 composition, for which the said polymer is either in the form of bulk polymer or in the form of a solution

or suspension.

It has likewise been found, unexpectedly, that the presence of microfibrils combined with mineral particles leads to a significant decrease in the maximum value of the tangent of the loss angle  $\tan \delta$ , under a deformation of less than 50% at room temperature, i.e. about 20°C.

It is recalled that the maximum of the tangent of the loss angle corresponds to the maximum of the curve obtained by determining the ratio of the moduli  $E''$  (viscous modulus) and  $E'$  (elastic modulus) as a function of the deformation of the sample under sinusoidal stress.

The tangent  $\delta$  gives an indication of the ability of the material to dissipate energy. The higher its value, the greater the dissipation of energy in the material.

In the known systems comprising lattices and microfibrils, for example, a decrease in rigidity has been noted from deformations of 1 to 5%. This phenomenon has been attributed to the rupture of the network of percolated microfibrils, i.e. to damage which should be accompanied by a dissipation of energy.

In the case of the present invention, a person skilled in the art would thus expect to observe an increase in the dissipation of energy resulting from

this very phenomenon. However, this was not the case.

An additional advantageous phenomenon was also observed, which was associated with the maximum value of  $\tan \delta$ , on passing the mechanical glass transition temperature (or main relaxation temperature a). This value of  $\tan \delta$  is obtained from the curve which measures the change in the real moduli  $E'$  and the imaginary moduli  $E''$  as a function of the temperature, at constant frequency, in a range of low sinusoidal deformation (less than 0.1%).

A person skilled in the art would normally have expected, as is usually the case when a filler is introduced into a polymer, to observe a decrease in the maximum value of  $\tan \delta$ . However, quite the opposite was observed: this value was at least conserved, if not increased.

Other advantages and characteristics of the present invention will emerge more clearly on reading the description, the examples and the figure which follow.

It should be noted that Figure 1 represents the change in the secant modulus as a function of the deformation, of a vulcanized elastomeric composition comprising the combination according to the invention, and of a vulcanized elastomer-based composition comprising only mineral particles.

Figure 2 represents the change in the ratio  $E''/E'$  as a function of the deformation, giving access to  $\tan \delta$ .

Figure 3 represents the change in the real  
5 modulus  $E'$  as a function of the deformation.

As has been mentioned previously, the combination according to the invention comprises microfibrils with a mean diameter of less than  $0.8 \mu\text{m}$ .

The microfibrils advantageously have a mean  
10 diameter of less than  $0.5 \mu\text{m}$ . The mean diameter is more particularly less than  $0.1 \mu\text{m}$ , preferably less than  $0.05 \mu\text{m}$ . The mean diameter of the microfibrils is preferably between  $0.5 \text{ nm}$  and  $20 \text{ nm}$  and even more preferably between  $5 \text{ nm}$  and  $20 \text{ nm}$ .

15 One important characteristic of the microfibrils of the invention is their form factor, which is defined as the ratio between the mean length of the microfibril  $L$  and its mean diameter  $D$  ( $L/D$ ). Thus, in the context of the present invention, the  
20 microfibrils have an  $L/D$  ratio of greater than or equal to 15, more particularly greater than or equal to 20 and preferably greater than or equal to 100.

The choice of microfibrils, in particular in terms of diameter and form factor, should be such that  
25 the mean length of the said microfibrils always remains less than  $30 \mu\text{m}$ .

The mean diameter can be measured, for example, by transmission electron microscopy (TEM). Depending on the dimensions of the fibre, the mean length can be determined, for example, by scanning electron microscopy (SEM) or by transmission electron microscopy (TEM).

According to one preferred embodiment of the invention, the combination comprises microfibrils with a mean diameter of less than 0.8  $\mu\text{m}$  and an L/D ratio of greater than or equal to 15, more particularly greater than or equal to 20, preferably greater than or equal to 100. Needless to say, the mean length of the microfibrils is less than 30  $\mu\text{m}$ .

Another even more preferred embodiment of the invention consists in using microfibrils with a mean diameter of between 0.5 nm and 20 nm. The mean diameter is more particularly between 5 nm and 20 nm. The form factor is greater than or equal to 15, more particularly greater than or equal to 20 and preferably greater than or equal to 100. Obviously, the mean length of the microfibrils is less than 30  $\mu\text{m}$ .

The sources of microfibrils having the characteristics mentioned previously are very varied.

According to a first possibility, they are chosen from ceramic microfibrils. For example, mention may be made of silicon carbide, silicon nitride or



boron nitride microfibrils.

Asbestos, titanate, alumina or aluminium and/or magnesium dihydroxycarbonate fibres are also suitable for use.

5           A second possibility consists in using carbon microfibrils which are optionally hollow.

          According to a third possibility, the microfibrils used are organic microfibrils. By way of example, mention may be made of polyvinyl alcohol,  
10   polyamide and cellulose microfibrils.

          When the microfibrils are cellulose microfibrils, they can be of plant origin, such as cellulose derived from plant parenchyma; of bacterial origin; or of animal origin, for instance cellulose  
15   such as tunicin, obtained from marine animals.

          According to one particularly advantageous variant of the invention, the combination comprises essentially amorphous cellulose microfibrils. The expressions "essentially amorphous" denotes  
20   microfibrils with a degree of crystallinity of less than or equal to 50%. This degree is preferably less than 50%. The degree of crystallinity is even more preferably greater than or equal to 15% and less than 50%.

25           The cellulose microfibrils used in the present invention are more particularly derived from

cells consisting of at least 80% by weight of primary walls. The amount of primary walls is preferably at least 85% by weight.

Such characteristics occur in particular with parenchymal cells. Sugar beet pulp, citrus fruits such as lemons, oranges and grapefruit, and most fruits and vegetables constitute examples of parenchyma.

Moreover, according to one particularly advantageous variant, the cellulose microfibrils are surface-charged with carboxylic acids and acidic polysaccharides alone or as a mixture.

The term "carboxylic acids" means simple carboxylic acids, as well as salts thereof. These acids are preferably chosen from uronic acids. The said uronic acids are more particularly galacturonic acid and glucuronic acid.

Acidic polysaccharides which may be mentioned are pectins which are more particularly polygalacturonic acids. These acidic polysaccharides can be present as a mixture with hemicelluloses.

Such cellulose microfibrils have been described in European patent application EP 726 356.

It should be noted that it would not constitute a departure from the context of the present invention to use cellulose microfibrils which do not have such surface charges, such as those obtained

according to the process described in patent EP 102 829. Moreover, it would be entirely conceivable to use cellulose microfibrils of this type, mixed with carboxylic acids and/or acidic polysaccharides as described above.

According to another possibility, the cellulose microfibrils can be mixed with at least one acid chosen from dithiodipropionic acid, tetrathiodipropionic acid or mercaptopropionic acid.

According to one particularly advantageous embodiment of the present invention, the cellulose microfibrils are obtained by carrying out the treatment which will be described below. This treatment is more particularly carried out on the pulp of plants with primary walls, such as, for example, beetroot pulp, after it has undergone a preliminary step of extraction of the sucrose, according to the methods known in the art.

This process thus consists in carrying out the following steps:

- (a) first acidic or basic extraction after which a first solid residue is recovered,
- (b) optionally, second extraction, carried out under alkaline conditions, of the first solid residue, after which a second solid residue is recovered,

- (c) washing of the first or second solid residue,
- (d) optionally, bleaching of the washed residue,
- (e) dilution of the third solid residue obtained after step (d) so as to obtain a solids content of between 2% and 10% by weight,
- (f) homogenization of the dilute suspension.

It should be noted that this process has been described in detail in European patent application EP 726 356 filed on 07/02/96, and reference may thus be made thereto if necessary. Example 20 of the said text in particular gives a method for preparing a suspension of particularly advantageous essentially amorphous cellulose microfibrils.

The cellulose microfibrils forming part of the combination according to the invention can be used in the form of a suspension obtained directly from the process for preparing the microfibrils.

They can also, advantageously, be used in a dry form. In this case, they will be redispersed before being placed in contact with the mineral particles.

It should be noted that in the case of cellulose microfibrils, a "dry" form denotes cellulose microfibrils with a solids content of at least 40% by weight. More particularly, the solids content is at least 60% by weight and is preferably at least 70% by weight.

The cellulose microfibrils forming part of the combination according to the invention can optionally be supplemented with at least one additive chosen, for example, from carboxylated cellulose, natural polysaccharides and polyols.

When the cellulose microfibrils are used in a dry form, they are preferably combined with at least one additive chosen from carboxylated cellulose, natural polysaccharides and polyols.

The carboxylated cellulose used as additive is, more particularly, carboxymethylcellulose. Cellulose is a polymer consisting of glucose monomer units. The carboxylic group is introduced in a manner which is known per se, by reacting chloroacetic acid with the cellulose. The degree of substitution corresponds to the number of carboxymethyl groups per glucose unit. The maximum theoretical degree is 3. The degree of substitution of the carboxymethylcellulose may be less than or equal to 0.95 (low degree of substitution), or greater than 0.95 (high degree of substitution). It is entirely conceivable to use cellulose microfibrils comprising both categories of carboxymethylcellulose.

The additive may also be a natural polysaccharide. This polysaccharide may be of bacterial, animal or plant origin. Polysaccharides are

polymers comprising oside units. Polysaccharides in anionic or nonionic form are preferably used.

Among the suitable anionic polysaccharides which may be mentioned, without any intention of being limited thereby, are xanthan, succinoglycanes, carrageenans and alginates, xanthan gum being preferred.

Among the nonionic polysaccharides which may be mentioned, for example, are galactomannans, for instance guar gum and carob gum. Starch and nonionic derivatives thereof are also suitable, as are nonionic cellulose derivatives.

Among the suitable polyols which may be mentioned most particularly are polyvinyl alcohols and polyalkylene glycols (polyethylene glycol, polypropylene glycol, mixture and copolymers).

When they are supplemented, the microfibrils can also comprise at least one co-additive chosen from:

- oside monomers or oligomers,
- compounds of formula  $(R^1R^2N)COA$ , in which formula  $R^1$  or  $R^2$ , which may be identical or different, represent hydrogen or a  $C_1-C_{10}$ , preferably  $C_1-C_3$ , alkyl radical, A represents hydrogen, a  $C_1-C_{10}$ , preferably  $C_1-C_3$ , alkyl radical or a group  $R^1R^2N$  with  $R^1$  and  $R^2$ , which may be identical or different, representing hydrogen or a  $C_1-C_{10}$ , preferably  $C_1-C_3$ , alkyl radical,

- cationic or amphoteric surfactants,  
it being possible for these co-additives to be used  
alone or as a mixture.

Among the oside monomers or oligomers which  
5 may be mentioned most particularly, and without any  
intention of being limiting, are sorbitol, sucrose and  
fructose.

As regards the compounds of the type  
(R'R''N)COA, the compounds comprising two amide functions  
10 are preferably used. Urea is preferably used.

Among the cationic surfactants which may be  
mentioned are cationic quaternary ammonium derivatives  
such as, for example, cationic imidazoline derivatives,  
alkyltrimethylammonium, dialkyldimethylammonium,  
15 alkyldimethylbenzylammonium or  
alkyldimethylethylammonium halides, and Quat esters.

Among the amphoteric surfactants which may be  
mentioned, without any intention of being limiting, are  
amphoteric alkylpolyamine derivatives, alkylbetaines,  
20 alkyldimethylbetaines, alkylamidopropylbetaines,  
alkylamidopropyldimethylbetaines,  
alkyltrimethylsulphobetaines, imidazoline derivatives  
such as alkyl amphotacetates, alkyl amphodiacetates,  
alkyl amphopropionates, alkyl amphodipropionates,  
25 alkylsultaines or alkylamidopropylhydroxysultaines, and  
the products of condensation of fatty acids and of

protein hydrolysates, it being possible for these compounds to be used alone or as a mixture.

The contents of additive and of co-additive, if the latter is present, can vary within a wide range.

- 5 However, in the case of essentially amorphous cellulose microfibrils, it is preferable for the total amounts of additive and optionally of co-additive to be not more than 50% by weight relative to the weight of cellulose microfibrils, additives and, optionally, co-additives.
- 10 The amounts are preferably less than or equal to 30% by weight relative to the weight of cellulose microfibrils, additive and, optionally, co-additive.

- However, the characteristics of such cellulose microfibrils which are in dry form, and the
- 15 preparation thereof are described in European patent application WO 98/02486 and WO98/02487, to which reference may be made for further details.

It is likewise conceivable to use cellulose microfibrils which have undergone a surface treatment.

- 20 Thus, by way of example, mention may be made of the process described in WO 97/12917. That document discloses cellulose microfibrils which are characterized in that at least 25%, in numerical terms, of the hydroxyl functions present at the surface of
- 25 these microfibrils are esterified with at least one organic compound comprising at least one function which



can react with the hydroxyl groups of cellulose.

The process for preparing such surface-modified microfibrils consists in:

- (a) dispersing the cellulose microfibrils in  
5 a liquid medium which does not destructure the cellulose microfibril,
- (b) adding to the dispersion an agent for esterifying the hydroxyl functions of cellulose, and optionally a catalyst and/or activator for the  
10 esterification reaction,
- (c) stopping the esterification reaction after the desired degree of esterification has been obtained,
- (d) extracting the partially esterified  
15 microfibrils from the dispersion.

The esterifying agent is more particularly an organic compound chosen from the group, comprising acetic, propionic, butyric, acrylic or methacrylic anhydrides or halides and the corresponding acids. It  
20 may likewise be conceivable to carry out such a process with at least one acid chosen from dithiodipropionic acid, tetrathiodipropionic acid or mercaptopropionic acid.

The catalyst for the esterification reaction  
25 is chosen from the group comprising basic catalysts and acidic catalysts, and more particularly inorganic

acids, organic acids and tertiary amines.

It is likewise possible to use microfibrils, and in particular cellulose microfibrils, which have been surface-treated such that they bear a polypyrrole coating. The process comprises the following steps:

- (a) a colloidal suspension of microfibrils, pyrrole and ferric chloride are placed in contact in distilled water,
- (b) this mixture is left to react at a temperature of between 5°C and room temperature,
- (c) the solids obtained are washed and the resulting solids are dispersed in water by means of ultrasound.

This process has been described in particular in European patent application EP 783 015.

Obviously, it would not constitute a departure from the context of the present invention to use microfibrils of different types.

The microfibrils thus defined are thus combined with at least one mineral particle.

The microfibrils can be combined with one or a mixture of mineral particles.

The particles size of the mineral particles varies within a wide range. However, mineral particles are used which, during the use of the combination in the polymer matrix, make it possible to obtain

dispersed particles with a mean diameter ranging from a few nanometres to several microns. For example, the mean diameter may be between 3 nm and 10  $\mu$ m and preferably between 3 nm and 5  $\mu$ m.

5                   According to a first variant, the mineral particles are chosen from the oxides, hydroxides and hydroxycarbonates, or combinations thereof, of elements from columns IIA, IIB, IIIB, IVA, IVB and VB of the Periodic Table of the Elements (published in the  
10   Supplément au Bulletin de la Société Chimique de France [Supplement to the Bulletin of the French Chemical Society], No. 1, January 1966), preferably titanium, aluminium, silicon, zinc, calcium and magnesium or mixtures thereof.

15                   Possible combinations which may be mentioned, without any intention of being limiting, are in particular mica, silicoaluminates, for instance clays, such as kaolin, for example.

                  It should be noted that these combinations  
20   can be used starting with a dry form which is redispersed before or during their use to prepare the combination according to the invention. It is likewise possible to use suspensions obtained directly from the process for preparing the said mineral particles,  
25   generally using a precipitation step. Working in this way makes it possible to dispense with the step for

redispersion of particles.

Thus, it is entirely conceivable to place the microfibrils in contact with a suspension of oxide, hydroxide and/or hydroxycarbonate particles, after the  
5 said precipitation step, or after the step of filtration and resuspension (mechanical or chemical disintegration).

It is likewise possible to use oxides, hydroxides and/or hydroxycarbonates which have  
10 undergone a high-temperature treatment (calcination). In this case, the microfibrils are introduced after this calcination step, in order to avoid any degradation thereof.

According to a second variant, the mineral  
15 particles are chosen from alkali metal or alkaline-earth metal carbonates, hydrogen carbonates and phosphates, or mixtures thereof. Alkaline-earth metal compounds, and more particularly calcium and magnesium compounds, are preferably used.

20 A third variant consists of mineral particles chosen from cerium and lanthanum compounds. In this respect, mention may be made in particular of sulphides and oxides, or mixtures thereof.

A fourth variant consists of silicon carbide  
25 particles.

Obviously, it would not constitute a

departure from the context of the present invention to use several types of mineral particle in the combination according to the invention.

Finally, a fifth variant of the invention consists in using carbon black particles as mineral particles, even though the classification of these particles as "mineral" rather represents an abuse of terminology.

It should be noted that it would also not constitute a departure from the context of the invention to use particles comprising carbon in their molecule, coated with at least one compound corresponding to the four abovementioned variants, i.e. with at least one compound chosen from oxides, hydroxides or hydroxycarbonates of elements from columns IIA, IIB, IIIB, IVA, IVB and VB of the Periodic Table of the Elements; alkali metal or alkaline-earth metal carbonates, hydrogen carbonates or phosphates; or silicon carbide.

According to one specific embodiment of the present invention, mineral particles with a BET specific surface of greater than  $30 \text{ m}^2/\text{g}$ , more particularly between  $50 \text{ m}^2/\text{g}$  and  $400 \text{ m}^2/\text{g}$ , are used. It should be noted that the BET specific surface is determined according to the Brunauer-Emmet-Teller method described in "The Journal of the American

Society", Vol. 60, page 309, February 1938 and corresponding to standard NF T 45007 (November 1987). The particles used in the present invention preferably have a specific surface of between 80 m<sup>2</sup>/g and 250 m<sup>2</sup>/g.

- 5 One particularly advantageous embodiment consists in using mineral particles chosen from oxides, hydroxides and hydroxycarbonates which have a specific surface in the range indicated previously. According to one even more advantageous embodiment of the invention, the
- 10 mineral particles are chosen from precipitated silicas, more particularly having a specific surface of between 110 m<sup>2</sup>/g and 230 m<sup>2</sup>/g, and for example between 140 m<sup>2</sup>/g and 220 m<sup>2</sup>/g.

- Moreover, mineral particles which have
- 15 undergone a total or partial prior surface treatment can be used. Examples which may be mentioned are surface treatments carried out on titanium dioxide with silica or a silica aluminate, or alternatively the treatment carried out on silica with polyethylene
- 20 glycol. Similarly, mention may be made of the partial surface treatment of calcium carbonate particles with a carboxylic acid.

- The amount of microfibrils in the combination is advantageously between 0.1 g and 100 g, more
- 25 particularly between 1 g and 10 g relative, to 100 g of mineral particles. Such a content is preferably between

2 g and 5 g per 100 g of mineral particles.

When the microfibrils comprise additives or co-additives, the ranges indicated above remain valid, with the exception that it relates to the total content of the microfibrils and of additives and co-additives.

A process for preparing a composition according to the invention will now be described. It consists in preparing a suspension comprising the abovementioned microfibrils and mineral particles, which is then dried.

Thus, in a first step, a suspension is prepared comprising the microfibrils, optionally in the presence of additives or co-additives, and the mineral particles.

Conventionally, a suspension is prepared in water. However, it is possible to replace all or some of the water with a dispersant liquid which is inert towards the mineral particles and microfibrils, and which preferably does not dissolve them. In addition, this dispersant is chosen such that it is compatible with the conditions for drying the suspension. Alcohols such as ethanol or methanol can be used more particularly.

Usually, the solids content of the suspension thus obtained, comprising the microfibrils and mineral particles, is between 10% and 40% by weight.

Although this is not obligatory, it may be preferable to carry out a homogenization step or any treatment allowing a disintegration of the particles and microfibrils, such as wet grinding or ultrasound treatment, for example.

In addition, it may be advantageous to introduce a stabiliser into the suspension. In this respect, mention may be made of hydrocolloids.

Once the suspension has been obtained, a drying operation is carried out on it.

Any conventional means can be used provided that the temperature reached by the combination during drying does not result in degradation of the components constituting it.

By way of illustration, the drying is carried out under conditions such that the temperature reached by the microfibrils/mineral particles combination is between room temperature and a temperature below 170°C, more particularly below 150°C and preferably below 120°C.

The drying is generally carried out under air but it is possible to carry it out under an inert atmosphere (nitrogen or rare gases).

Thus, the suspension can be dried in any known type of machine, such as ovens on a conveyor belt, with or without induction, radiative or non-



radiative, rotary ovens, fluidized beds or lyophilizers.

According to one specific embodiment of the invention, the drying is carried out by atomization, i.e. by spraying the suspension in a hot atmosphere (spray-drying). The atomization can be carried out using any sprayer which is known per se, for example using a liquid pressure nozzle, or the like. It is also possible to use so-called turbine atomizers. For the various spraying techniques which may be used in the present process, reference can be made in particular to the reference text by MASTERS entitled "SPRAY-DRYING" (second edition, 1976, published by George Godwin - London).

It will be noted that the drying operation can also be carried out by atomization using a "flash" reactor, for example of the type described in particular in French patent applications Nos. 2 257 326, 2 419 754 and 2 431 231. In this case, the treating gases (hot gases) are driven in a spiral movement and flow in a vortex well. The mixture to be dried is injected along a trajectory merged with the axis of symmetry of the spiral trajectories of the said gases, thereby making it possible to entirely transfer the amount of movement of the gases to the mixture to be treated. The gases thus serve two purposes: firstly,

the spraying, i.e. the conversion into fine particles of the initial mixture, and secondly the drying of the particles obtained. Moreover, the extremely short residence time (generally less than 0.1 second approximately) of the particles in the reactor has the advantage, inter alia, of limiting any risks of over heating after too long a contact with the hot gases. As regards the flash reactor mentioned above reference may be made in particular to Figure 1 of French patent application 2 431 321.

At the end of this step, the combination according to the invention is obtained, which is in the dry (solid) form. It should be noted that the combination can have a residual content of water or dispersant liquid. This residual content is such that the appearance of the individualized particles in the combination is conserved. It consequently depends greatly on the nature of each of the constituent elements of the combination. By way of example, this residual content is generally less than or equal to 20%, preferably less than or equal to 10%.

At this stage the combination obtained by drying can be in the form of substantially spherical beads. This variant is particularly advantageous when the mineral particles are chosen from oxides. Reference may be made to the conditions described in patent

applications EP 520 862, EP 670 813 and EP 670 814.

The resulting product may, if necessary and so as to limit the powdering phenomenon, be placed in contact with a mixture comprising a mineral oil and optionally a polymer. The mineral oil may be, for example, a naphthenic oil. The polymer is preferably a polymer or copolymer of ethylene, of propylene and optionally of a diene (such as hexadiene or ethylidenenorbornene), in which the ethylene content is from 60% to 90% by weight, the propylene content is from 10% to 35% by weight and the diene content, if a diene is present, is from 2% to 10% by weight. Reference may be made in particular to international patent application PCT/GB96/03222.

The dried product can, if necessary, undergo a step of grinding or of disintegration.

If so desired it is possible to carry out a step of shaping of the dried product, to make it more practical to use. Thus, it is possible to carry out, inter alia, a granulation, a compaction or an extrusion.

These operations are entirely conventional to those skilled in the art. They generally consist, in the case of granulation or extrusion, in adding the required amount of a binder chosen from compounds that are compatible with the compositions in which the

combination is subsequently used, in granulating or extruding the mixture in conventional machines, and then in drying the resulting product, if necessary.

As regards compaction, this is usually  
5 carried out by subjecting the combination to high pressure, optionally in the presence of a suitable binder depending on the subsequent use of this combination.

Binders which may be mentioned in particular  
10 are polyethylene glycol and stearic acid.

The combination according to the invention,  
optionally after having been formulated, is usually in a dry form in which the size of the particles of which it is composed is between 0.5  $\mu\text{m}$  and 5 mm and more  
15 particularly between 5  $\mu\text{m}$  and 5mm.

The combination according to the invention can be used in many fields.

The combination according to the invention is advantageously used in compositions based on polymers  
20 or copolymers, in particular as reinforcing fillers. In the text hereinbelow, for the purposes of simplicity, reference will be made merely to polymers, bearing in mind that this term covers both polymers and copolymers, alloys thereof or blends thereof.

25 Among the suitable polymers which may be mentioned are elastomers, polymers or copolymers with a

glass transition temperature of between  $-150^{\circ}\text{C}$  and  $+20^{\circ}\text{C}$ .

Suitable compounds which may be mentioned, without, however, any intention of being limited thereto, are synthetic elastomers or (co)polymers or natural products. For example, mention may be made of natural rubber, polymers or copolymers derived from aliphatic or aromatic monomers, comprising at least one unsaturation, such as, in particular, ethylene, propylene, butadiene, isoprene or styrene; polybutyl acrylate, or combinations thereof. Silicone elastomers may similarly be suitable for carrying out the present invention, as may halogenated polymers including PVC and halogenated elastomers.

According to the present invention, a mixture comprising the combination of microfibrils and mineral particles, the polymer and, where appropriate, additives that are suitable for the application, is formulated. Thus, the polymer compositions may comprise vulcanization ingredients in the specific case of elastomers, coupling agents, plasticizers, stabilizers, lubricants, pigments, etc.

The proportion by volume represented by the combination according to the invention in the polymer composition may vary within a wide range, or even, in certain applications may represent a larger amount than

the polymer. However, more particularly, the volume of the combination according to the invention represents 0.1% to 50% relative to the volume of polymer, optionally comprising the abovementioned additives.

- 5 This volume preferably represents 0.1% to 25% of the volume of polymer, optionally comprising the abovementioned additives.

It should be noted, and this constitutes an additional advantage of the present invention, that the  
10 combination according to the invention can be carried out, indifferently, with a bulk polymer, with a polymer latex or with a polymer solution. It is pointed out that the term "latex" means suspensions of polymer in water or in any other suitable dispersant liquid.

- 15 The reason for this is that, unlike the known agents based on fibres or microfibrils, the combination according to the invention is entirely suited to the polymer composition and disperses fully therein, irrespective of the form of the composition.

20 The use and formulation of the polymer comprising the combination according to the invention are conventional in the field. They do not require any specific equipment or procedures.

Thus, when the elastomer is not in latex  
25 form, a homogeneous blend of the combination according to the invention, of the elastomer and of the additives

is prepared by means, inter alia, of any known type of blender according to implementation procedures that are well known to those skilled in the art.

The said blend is formulated by moulding or  
5 extrusion in particular, and, if necessary, a heat treatment is carried out at a temperature below the degradation temperature of the combination according to the invention. This is more particularly the case for the vulcanization of elastomers. The operating  
10 temperature is usually less than 170°C.

When the polymer is in the form of a latex or solution, the blending of the latex or solution with the combination according to the invention is carried out, followed by a conventional removal of the liquid  
15 phase. The resulting product can then be formulated in a conventional manner.

When the polymer is a thermoplastic polymer, the homogeneous blend of the combination, of the polymer and of the additives can be obtained by any  
20 means known to those skilled in the art which allows the incorporation of mineral fillers into a thermoplastic polymer, in particular by means of a twin-screw extruder.

The said blend is then formulated by  
25 calendering or injection, in particular.

The polymer-based articles comprising the

combination according to the invention, which are thus obtained, can be used as technical plastics or technical elastomers, in applications as varied as in the motor vehicle field.

5           Thus, they can be used as floor coverings, engine supports, vehicle caterpillar-track components, shoe soles, cable-car rollers, seal for household electrical appliances, sheathing, cabling and transmission belts.

10           Thus, the present invention makes it possible to obtain articles in which the polymer is an elastomer or an alloy or blend of elastomers, and preferably vulcanized, which can be used in any part of a tyre.

15           In this specific case, it should be noted that the content of combination according to the invention is such that the content of microfibrils in the part of the tyre under consideration is between 0.1 g and 20 g per 100 g of elastomers, polymers or copolymers.

20           Finally, the articles according to the invention can find applications as battery separators.

Concrete but in no way limiting examples of the invention will now be given.

#### **EXAMPLE 1**

25           This example illustrates the preparation of a combination according to the invention, comprising



precipitated silica and cellulose microfibrils.

Example 12 of European patent EP 520 862 is carried out, until a precipitated silica pulp is obtained, which is filtered and washed using a filter  
5 press so as to recover a silica cake whose loss on ignition is 79% (21% content of silica).

This cake is then fluidized by mechanical and chemical action via addition of an amount of sodium aluminate corresponding to an Al/SiO<sub>2</sub> weight ratio of  
10 3000 ppm. The suspension thus obtained thus has a pH of 6.3 and a precipitated silica content of close to 21% by mass.

2419 g of water and 1300 g of cellulose microfibril pulp are added to 2641 g of the above  
15 suspension.

This pulp is obtained according to the process described in patent application EP 726 356, in accordance with Example 20 before concentration, except  
20 that the solids content of the suspension is 2.3%.

The suspension of silica and microfibrils is homogenized using a Rayneri blender in order to obtain a suspension with a precipitated silica content of 9%. The microfibrils/silica mass ratio is about 5.4%.

This suspension is atomized on an APV turbine  
25 atomizer.

The product obtained has:

- \* a BET surface of  $165 \text{ m}^2/\text{g}$
- \* a total pore volume of  $3.2 \text{ ml/g}$
- \* a median pore diameter of  $24 \text{ nm}$ .

N.B.: the pore volume is measured by mercury

- 5 porosimetry, the pore diameters being calculated by means of the Washburn relationship with a contact angle of  $140^\circ$  and a surface tension of  $484 \text{ Dynes/cm}$ . The porosity measurements are carried out on products dried at  $150^\circ\text{C}$  under a pressure of  $1 \text{ Pa}$ . The pore volume  $V_p$
- 10 relates to the pores with a radius of less than  $1 \mu\text{m}$ ; the median pore diameter corresponds to the maximum of the derivative of the curve  $V = f(\log d)$  for the portion relating to the mesopores (course of porosity for the pores with a diameter of less than  $0.1 \mu\text{m}$ ).

## 15 **EXAMPLE 2**

The aim of this example is to obtain particles of precipitated silica alone (reference).

- 6205 g of water are added to 4797 g of suspension described in Example 1 in order to form a
- 20 suspension with a 9% content of precipitated silica.

This suspension is atomized on an APV turbine atomizer under the same conditions as in the above example.

The product obtained has:

- 25
- \* a BET surface of  $165 \text{ m}^2/\text{g}$
  - \* a total pore volume of  $3.5 \text{ ml/g}$

\* a median pore diameter of 25 nm.

It is observed that the products of Examples 1 and 2 have similar textures and surfaces.

### EXAMPLE 3

5           The aim of this example is to evaluate the properties of elastomers comprising the products obtained from Example 1 (composition A - composition comprising the combination according to the invention) and Example 2 (composition B - composition based on  
10 precipitated silica alone).

Two elastomer compositions below are prepared:

	A	B
SBR(*)	100	100
15 Silica of Ex. 2	-	58
combination of Ex. 1	60.9	-
Si69(**)	4.6	4.6
Diphenylguanidine	1.45	1.45
Stearic acid	1.1	1.1
20 Zinc oxide	1.82	1.82
Antioxidant (***)	1.45	1.45
Sulphenamide (****)	1.3	1.3
Sulphur	1.1	1.1

25   The amounts are expressed by weight per 100 parts of elastomer.

(\*) styrene-butadiene copolymer synthesized in solution (SBR Buna VSL 5525-1/Bayer) containing 27.3% oil.

(\*\*) Si69 is bis(triethoxysilylpropyl) tetrasulphide (Degussa).

(\*\*\*) Antioxidant: N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine.

5 (\*\*\*\*) Sulphenamide: N-cyclohexyl-2-benzothiazole sulphenamide.

Each composition is prepared by thermomechanical working in a 1-litre internal blender, in two steps, for an average paddle speed of 80 rpm until a temperature of 160°C is reached at the end of each of these two steps, and followed by a finishing step in an external mixer. The vulcanization of the compositions is adapted to the vulcanization kinetics of each blend.

15 The physical properties of the blends are given in the table below.

	Properties	A	B
20 "Crude" properties (before vulcanization)	ML1+4 (Mooney "points")	64	61
	shrinkage	20%	27%
Properties of the vulcanizates	100% modulus (MPa)	4.1	2.5
	300% modulus (MPa)	13.9	13
	Deformation at break	420%	410%
	Breaking stress (MPa)	20.9	18.9

25

The measurements are carried out according to the

following methods:

- Mooney viscosity: ML1+4 on crude blend according to standard NF T 43005

- Shrinkage:

- 5 Apparatus: An MAL ATC 01 roll mixer is used (in calendering - front roller-rear roller speed is 18 rpm)  
Temperature: 20°C  
Guide spacing: 10 cm
- 10 Roller spacing: 2 cm (flange about 1 cm).
- Procedure: Leave 220 g of blends to sleeve-couple for 30 seconds. Chop 10 times to 2/3 (5 on the left - 5 on the right). After 2
- 15 minutes, separate the rollers until the flange completely disappears. Couple the blend throughout the width. Leave the rubber strip to stand for 24 hours on a talc-dusted table and measure the length
- 20 of the strip.  
The shrinkage is then given by  $(D-L)/D \cdot 100$ , in which formula D represents the circumference of the roller and L represents the length of
- 25 the strip after leaving to stand for 24 hours.

Tension: The moduli are measured on the vulcanizates according to standard NF T46002. It should be noted that the 100% modulus, in the rubber sector, refers to the stress measured at 100% tensile deformation: the 300% modulus refers to the stress measured at 300% tensile deformation.

From the above summary table, it can be seen that the composition containing the combination of silica and microfibrils according to the invention leads to a markedly higher mechanical stress at about 100% deformation compared with the reference composition. This indicates that the microfibrils have been distributed homogeneously in the elastomer.

In addition, as illustrated in Figure 1, which shows the change of the secant modulus (defined as the ratio of the stress at a given deformation to the deformation) as a function of the deformation, the moduli are improved up to more than 300% deformation.

It is noteworthy and entirely unexpected for a person skilled in the art to find that the gain in modulus of the elastomeric composition comprising the combination according to the invention is achieved without negatively affecting the rheology of the crude blend, or the breaking strength or elongation at break

of the vulcanized blend.

Moreover, the blend thus obtained has better shrinkage strength than the control composition, comprising only silica, which is an advantage in terms of formulation by extrusion or calendering, in particular.

#### EXAMPLE 4

The aim of this invention is to show the influence of the combination according to the invention on the change in the viscoelastic properties and in particular the tangent of the loss angle ( $\tan \delta$ ), as a function of the deformation and temperature.

Measurement method: the real modulus ( $E'$ ) and imaginary modulus ( $E''$ ), and also the tangent of the loss angle ( $\tan \delta$ ), defined as the ratio of  $E''$  to  $E'$ , were measured at different degrees of deformation, on a mechanical spectrometry machine (VA2000 Viscoanalyser from Metravib RDS).

The test conditions are as follows:

- The test samples are of parallelepipedal form (length 6 mm, width 6 mm, thickness 2.5 mm approximately).
- The test sample is subjected to a test at 23°C which is similar to a tensile test, consisting in subjecting the test sample to increasing stages of force and thus of deformation. During each stage,

a sinusoidal deformation with a frequency of 5 Hz and an amplitude of 10 microns is applied to the test sample, thus making it possible to measure the  $E'$  and  $E''$  moduli and the  $\tan \delta$ .

5           Compositions A and B described in Example 3 were thus tested after vulcanization in accordance with the above procedure.

It is found, as shown in Figure 2, that the maximum  $\tan \delta$  value of composition A, containing  
10 cellulose microfibrils introduced into the elastomer by means of the combination according to the invention, is 0.30, while that of composition B is 0.32.

This result is entirely unexpected. The reason for this is that in the known systems comprising  
15 lattices and microfibrils, a decrease in rigidity was observed from deformations of 1 to 5%. This phenomenon is attributed by those skilled in the art to the rupture of a network of percolated fibres, and thus to a damage. This damage is normally accompanied by a  
20 dissipation of energy, and thus an increase in  $\tan \delta$ .

The lower value of the elastic modulus  $E'$  of composition A, at very low deformation, and the increase in this value at higher deformation relative to the values obtained with composition B should also  
25 be observed in Figure 3.

An additional advantageous phenomenon



associated with the maximum value of the  $\tan \delta$  was also observed on passing the mechanical glass transition temperature (or main relaxation temperature  $\alpha$ ). This  $\tan \delta$  value is obtained from the curve measuring the  
5 change in the real moduli  $E'$  and imaginary moduli  $E''$  as a function of the temperature at constant frequency, in a range of low deformation (less than 0.1%).

It is found that the maximum value of  $\tan \delta$  for composition A on passing the mechanical glass  
10 transition temperature (observation at 10 Hz at a main relaxation temperature  $\alpha$ ) is 0.77, whereas that of composition B is 0.76.

A person skilled in the art would normally have expected to observe a decrease in the maximum  
15 tangent value on passing the mechanical glass transition. However, it was noted that this value was at least conserved, or even increased.

This result is surprising since, in composition A, the proportion of polymer which crosses  
20 the mechanical glass transition is lower on account of the addition of fibres, than in composition B.

A decrease in the maximum value of  $\tan \delta$  on passing the mechanical glass transition should thus have been observed.

25 The entirely specific behaviour of composition A in Examples 2 and 3 indicates, in an

obvious manner to those skilled in the art, that a combination according to the invention of a reinforcing mineral filler (for example a dispersible precipitated silica) and of cellulose microfibrils (for example cellulose parenchymas obtained from plant products) can be used so as to improve the compromise of properties for virtually all the parts of a tyre.

#### EXAMPLE 5

The aim of this example is to evaluate the properties of elastomers comprising the products obtained from Example 1 (composition C) and Example 2 (composition D) in a formula based on natural rubber and polybutadiene.

Two elastomeric compositions below are prepared:

	C	D
NR SMR 10 (*)	50	50
BR(**)	50	50
Silica of Ex. 2	-	50
combination of Ex. 1	52.5	-
Si69(***)	4	4
Oil (****)	7	7
Stearic acid	1	1
Zinc oxide	3	3
Sulphenamide (***)	1	1
Sulphur	2	2

The amounts are expressed by weight per 100 parts of

elastomer.

(\*) Natural rubber.

(\*\*) Polybutadiene: Cariflex BR 1220 L (Shell Chimie)

(\*\*\*) Si69 and sulphenamide: see Example 3

5 (\*\*\*\*) Oil: Ferumil oil from Shell.

Each composition is prepared by thermomechanical working in a 1-litre internal blender, in one step, for an average paddle speed of 80 rpm, until a temperature of 160°C is reached at the end of  
10 the step, and followed by a step of acceleration and finishing in an external mixer. The vulcanization of the compositions is adapted to the vulcanization kinetics of each blend.

The physical properties of the blends are  
15 given in the table below.

	Properties	C	D
20 "Crude" properties (before vulcanization)	ML1+4 (Mooney "points")	76	80
Properties of the vulcanizates	10% modulus (MPa)	0.46	0.39
	100% modulus (MPa)	1.6	1.1
	300% modulus (MPa)	5	3.4
	Deformation at break	620%	625%
	Breaking stress (MPa)	13.2	10.8
	Shore A 15s	51	44
	Tearing (kN/m)	34.9	37.2

	Abrasion (mm <sup>3</sup> )	56	65
	G', (MPa)	2.2	1.4
	Tan $\delta$ max	0.2	0.24

The measurements are carried out according to the following methods:

- tension: as in Example 3 according to standard  
5 NFT 46002
- trouser tear test: according to standard NF  
T46035
- abrasion: according to standard NF T46012
- G': real modulus, measured by a test of  
10 simple dynamic shear carried out at increasing deformation, at 5 Hz and at 23°C. G' is measured at 0.01% deformation.
- tan  $\delta$  max: the maximum of the tangent of the loss  
15 angle, measured by a test of simple dynamic shear carried out at increasing deformation, at 5 Hz and at 23°C.  
Max tan  $\delta$  corresponds to the maximum value reached by tan  $\delta$  during a  
20 deformation scanning.

From the summary table, it is found that the composition containing the combination of silica and microfibrils according to the invention (composition C) leads to markedly higher mechanical stresses at 10, 100

and 300% deformation compared with the reference composition (D) and to an abrasion strength and a tear strength that are significantly higher than those of the reference composition.

5           It is noteworthy and entirely unexpected for those skilled in the art to observe that the gain in modulus of the elastomeric composition comprising the combination according to the invention is achieved without negatively affecting the rheology of the crude  
10   blend, or the breaking strength or elongation at break of the vulcanized blend. On the contrary, it is found that the composition containing the combination has a lower viscosity than the reference composition (D).

          Moreover, the blend thus obtained shows  
15   dynamic behaviour which is distinguished from that of the reference composition, comprising only silica, by a higher rigidity at low deformation and a lower maximum dissipation, which is an advantage in tyre applications, in particular for the side walls.

#### 20   **EXAMPLE 6**

          The aim of this example is to evaluate the properties of elastomers comprising the products obtained from Example 1 (composition E) and Example 2 (composition F) compared with an elastomer comprising  
25   reinforcing carbon black (composition G).

          Three elastomeric compositions below are

prepared:

	E	F	G
NR SMR 10(*)	100	100	100
Silica of Ex. 2	-	50	-
5 Combination of Ex. 1	52.5	-	-
N 234 (**)	-	-	50
Si69(*)	5.25	5.25	-
Wax (***)	1	1	1
Stearic acid	3.75	3.75	3
10 Zinc oxide	4	4	4
Antioxidant (****)	2	2	2
Sulphenamide (*)	2.37	2.37	1.25
Sulphur	1.75	1.75	1.75

15 The amounts are expressed by weight per 100 parts of elastomer.

(\*) see Example 5,

(\*\*) N 234 : carbon black (Cabot),

(\*\*\*) Wax: Microwax 2000,

20 (\*\*\*\*) Antioxidant: N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine.

Each composition is prepared by thermomechanical working in a 1-litre internal blender, in one step, for an average paddle speed of 80 rpm, until a temperature of 160°C is reached at the end of the step, and followed by a step of acceleration and finishing on an external mixer. The vulcanization of the compositions is adapted to the vulcanization

kinetics of each blend.

The physical properties of the blends are given in the table below.

	Properties	E	F	G
5 "Crude"	ML1+4 (Mooney	48	51	54
properties	"points")			
Properties	10% modulus (MPa)	0.77	0.59	0.67
of the	100% modulus (MPa)	4.1	3.1	3
vulcanizates	300% modulus (MPa)	15.6	15.5	15.9
	Deformation at break	491%	497%	513%
	Breaking stress (MPa)	28.7	29.9	32.4
	Shore A 15s	66	63	62
	Tearing (kN/m)	11.6	10	12.5
	G' (MPa)	3.2	2.8	6.9
10	Tan $\delta$ max	0.1	0.09	0.22

The measurements are carried out according to the same methods as in Example 5.

From the summary table, it is observed that the composition containing the combination of silica and microfibrils according to the invention (composition E) leads to a hardness and to mechanical stresses that are markedly higher at 10 and 100% deformation compared with the reference compositions (F and G), and does so without negatively affecting the rheology of the crude blend or the breaking strength, elongation at break or tear strength of the vulcanized blend.

Moreover, the blend containing the combination of silica and microfibrils (E) shows dynamic behaviour which is comparable with that of the silica-based reference composition (F) but which is distinguished from that of the composition based on carbon black (G) by a higher rigidity at low deformation and a lower maximum dissipation, which is an advantage in tyre applications, in particular for heavy goods vehicles.